

Quantitative Validation of Ames IR Intensity and New Line Lists for $^{32/33/34}\text{S}^{16}\text{O}_2$, $^{32}\text{S}^{18}\text{O}_2$ and $^{16}\text{O}^{32}\text{S}^{18}\text{O}$

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Abstract

The quality of Ames-296K SO₂ Infrared (IR) line list intensities is first validated by quantitative exploration of several dipole moment surfaces (DMSs) and partition sum convergence. The DMSs are computed with several of Dunning's correlation-consistent basis sets and their vibrational dependence are compared to the empirical model derived from Stark effect experiments reported by D. Patel, D. Margolese, and T.R. Dyke [J.Chem.Phys. **70**, 2740 (1979)]. The effective dipole deviations from the DMS adopted in the Ames IR lists is 0.2-0.4% for vibrational states up to 3v₃. The vibrational dependence of the dipole moment is also in good agreement, except for nv₁. Partition sum convergence at 296K is confirmed by new calculations with rotational quantum number *J* up to 150 and upper state *E'* up to 8000 cm⁻¹. The isotopologue consistency of the Ames IR line lists is superior relative to the regular Effective Hamiltonian (EH) models and Effective Dipole Moment (EDM) models. The v₁+v₂ and v₂+v₃ intensity consistency check reveals the recently reported experimental intensities need significant improvement or re-analysis. After the accuracy, convergence, and isotopologue consistency have been confirmed, the theoretical Ames-296K intensities are combined with the experimental line positions or EH models that experimental spectroscopists published after 2009. Three high-resolution IR line sets are reported for the ^{32/33/34}S¹⁶O₂, ³²S¹⁸O₂ and ¹⁶O³²S¹⁸O isotopologues: (1) the "New Lines Sets" include experimentally measured line positions; (2) the "Expanded Line Sets" include possible transitions among new rovibrational levels assigned in experiments and ground state (GS) levels predicted by reliable EH models; (3) the "Ames + MARVEL Sets" include possible transitions among all those levels reported in a recent MARVEL analysis. [Tóbiás *et al*, JQSRT **208**, 152 (2018)]. Compared to the limited data in High-resolution TRANsmision molecular absorption database (HITRAN), these line sets have significantly improved the data coverage up to 4000 cm⁻¹. Some missing bands can be traced to the unpublished experimental data. The isotopologue consistency of these line sets will help identify the uncertainties and defects in the experimental EH and EDM models. These line sets are good candidates for the next HITRAN update, if line shape parameters are available. The line sets can be downloaded from supplementary files or from the Ames Molecular Spectroscopic Database at <http://huang.seti.org>.

1. Introduction

Since 2009, new SO₂ Infrared (IR) measurements and analyses have been carried out by the Ulenikov group,[1–20] Blake, Flaud, Lafferty[21,22], Perrin [23] and their co-workers, especially in the last two years (2016-2017). Many new IR bands were measured and reported for the first time in high-resolution with quantum number assignments for part or a majority of the $^{32/33/34}\text{S}^{16}\text{O}_2$, $^{32}\text{S}^{18}\text{O}_2$, and $^{16}\text{O}^{32}\text{S}^{18}\text{O}$ transitions. They significantly improved the high-resolution SO₂ IR data coverage. Unfortunately, these contributions did not get into the latest updates of the *high resolution transmission* molecular absorption database, i.e. HITRAN2016.[24] One reason is that the intensities were not directly reported or not readily available. The absolute IR intensity only can be found in 2017 Ulenikov *et al* [12] for the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of 4 isotopologues: $^{32/34}\text{S}^{16}\text{O}_2$, $^{32}\text{S}^{18}\text{O}_2$ and $^{16}\text{O}^{32}\text{S}^{18}\text{O}$.

Since 2014, our group at NASA Ames has published a series of SO₂ studies [25–28] reporting IR line lists computed on highly accurate potential energy surfaces (PES) we empirically refined using reliable high-resolution experimental data, i.e. the rovibrational energy levels derived from IR transitions (with $ierr \geq 4$) in HITRAN2012.[29] The index “ $ierr \geq 4$ ” means the line position uncertainty is less than 0.001 cm^{-1} .[30] The prediction accuracy of the Ames line lists is $0.01 - 0.02 \text{ cm}^{-1}$ for line positions and better than 90-95% for line intensities, as demonstrated in intensity comparisons[25,26] and mixed-isotopologue IR analysis.[27] Most recently, the Ames-296K IR lists have been re-computed for all 30 isotopologues related to the $^{32/33/34/35/36}\text{S}$ and $^{16/17/18}\text{O}$ isotopes, with $J=0-75$ and $E' < 8000 \text{ cm}^{-1}$.[31] The reliable and highly consistent IR intensities can be combined with the experimental data to generate new IR line lists to improve databases and facilitate atmospheric and (exo)planetary IR analysis and simulations, given appropriate line shape and broadening parameters are available.[32–35]

Compared to the state-of-the-art PES accuracy, the quality of our CCSD(T)/aug-cc-pV(Q+d)Z dipole moment surface (DMS) [25] has not been quantitatively validated. Compared to the $^{32}\text{S}^{16}\text{O}_2$ IR line list published with the ExoMol group [28], the Ames-296K IR line lists have limited coverage along J and wavenumber range. Therefore, before combining with experimental data, it is necessary to carry out convergence tests for partition sums. Sections 2 and 3 first present the results of these investigations. Section 4 discusses the isotopologue consistency of SO₂ EH models. Then Section 5 compares the isotopologue consistency of Ames IR line intensity vs. the inconsistency of experimental intensities of $\nu_1+\nu_2$ and $\nu_2+\nu_3$.[12] In the end, we introduce three sets of SO₂ IR line lists for 5 isotopologues in Sections 6 and 7, which are followed by conclusions.

In this paper, SO₂ isotopologues are labeled with 3-digit integers taken from the S and O isotope masses, in the order of O-S-O. This is also the regular labels used by other spectroscopists for SO₂ or CO₂ isotopologues. The main isotopologue $^{32}\text{S}^{16}\text{O}_2$ is denoted “626”, $^{33}\text{S}^{16}\text{O}_2$ is denoted “636”, $^{34}\text{S}^{16}\text{O}_2$ is denoted “646”, $^{32}\text{S}^{18}\text{O}_2$ is denoted “828”, and $^{16}\text{O}^{32}\text{S}^{18}\text{O}$ is denoted “628”. Please note that, in the figures and text, all Ames line intensities are at 296K with 100% abundances. They are not scaled by terrestrial or any other abundances.

2. SO₂ DMS: basis set effects and vibrational dependence

Details of the Ames PES refinement, dipole moment surface (DMS), and IR line list calculations can be found in Refs.[25,26], so they are not repeated here. In short, the Ames SO₂ DMS was fit from 3638 CCSD(T)/aug-cc-pV(Q+d)Z finite field dipoles computed in the range of $0 - 60,000 \text{ cm}^{-1}$. A permutation

invariant basis is adopted in the pseudo-point-charge-on-nuclei model. For the ~2900 points below 30,000 cm^{-1} , the average fitting error and relative fitting error are $1.8\text{E-}5$ a.u. and 0.010%. To study the *ab initio* basis set effect on the DMS, CCSD(T) finite field dipole calculations are carried out on the same geometry grid using MOLPRO 2015.1 [36]. The same field strength is applied. The following basis sets are used: aug-cc-pV(Q+d)Z (*avqdz*), aug-cc-pV(5+d)Z (*av5dz*), aug-cc-pCVQZ (*acvqz*), aug-cc-pwCVQZ (*awcvqz*), and d-aug-cc-pV(Q+d)Z (*davqdz*), with abbreviations in parentheses. Core-correlation effects are included in the *acvqz* and *awcvqz* calculations. The last basis set, *davqdz*, is the combination of d-aug-cc-pVQZ basis for O atom and aug-cc-pV(Q+d)Z basis for S atom.

It turns out that not all of the computed dipoles are reliable. The “outliers” are determined by cross check among the 5 dipoles at each geometry. At one geometry, there may be just 1 outlier in the 5 dipole values, but this point must be removed to keep the consistency of the new DMS fits. After the check, dipoles of 3477 points are fed to the same least-squares fitting program, with previous fitting weight setting. Fitting accuracy is reported in Table 1. The new DMS fits are comparable to the original “Published” DMS. These new DMS are used in the VTET program [37] to compute 5 different 296K IR line lists using the same set of $J=0-75$ rovibrational wavefunctions acquired from the Ames-Pre2 PES.[27] The differences among these 296K IR line lists are 100% the result of the *ab initio* one-particle basis sets. Note the difference between the “Published” DMS and the “*avqdz*” DMS is the removal of more than 100 dipoles at higher energy range.

Table 1. Six Ames SO_2 DMS fits, fitting accuracy in 0 – 30000 cm^{-1} . The vibrationally averaged (effective) dipole of ground state (GS), μ_{000} , are compared to the Experimental value $\mu_{000}=1.63305(4)$ D.

DMS	Fitting deviation		Effective Dipole of GS	
	$ \delta\mu\% _{\text{avg}}$	$ \delta\mu _{\text{avg}}$ (a.u.)	μ_{000} (Debye)	μ_{000} deviation
Published ^{&}	0.010%	$1.8\text{E-}5$	1.6362521	0.20%
<i>avqdz</i>	0.005%	$0.8\text{E-}5$	1.6362532	0.20%
<i>av5dz</i>	0.005%	$0.8\text{E-}5$	1.6340445	0.06%
<i>acvqz</i>	0.017%	$2.8\text{E-}5$	1.6412830	0.50%
<i>awcvqz</i>	0.012%	$1.8\text{E-}5$	1.6403576	0.45%
<i>davqdz</i>	0.044%	$5.8\text{E-}5$	1.6350176	0.12%
Expt.[38]			1.63305(4)	

[&] The DMS used in Refs.25-28, it was also based on CCSD(T)/aug-cc-pV(Q+d)Z dipoles.

In 1979, Patel, Margolese and Dyke [38] reported that Stark effect measurements gave the dipole for the SO_2 vibrational ground state (GS) $\mu_{000} = 1.63305(4)$ D (Debye). They summarized an empirical formula to estimate the dipole of vibrational excited states:

$$\begin{aligned} \mu_{v_1v_2v_3} = & 1.62673 + 0.00017 \cdot (v_1+0.5) - 0.00684 \cdot (v_2+0.5) + 0.01943 \cdot (v_3+0.5) - 0.00002 \cdot (v_1+0.5)^2 \\ & - 0.00003 \cdot (v_2+0.5)^2 + 0.00002 \cdot (v_1+0.5) \cdot (v_2+0.5) - 0.00012 \cdot (v_2+0.5) \cdot (v_3+0.5) \end{aligned} \quad (1)$$

where v_1 , v_2 , v_3 are the vibrational quanta for symmetric stretch, bending, and anti-symmetric stretch, respectively. These are “real” dipoles, i.e. vibrationally averaged. Not the static dipole given by the DMS fits at PES global minimum.

In order to make an apples-to-apples comparison, we need to perform a SPFIT/SPCAT [39–41] analysis. Pure rotational transitions within a specific vibrational state (including the GS) are extracted from the

Ames-296K IR line list of $^{32}\text{S}^{16}\text{O}_2$ (626), and fit to an EH model. Then the SPCAT program uses the fitted EH parameters, together with an adjustable effective dipole term, to predict the intensity of $J=1/0 \leftarrow J=1/0$ lines. Those lines are the main ones included in the experimental paper. When the intensity difference between SPCAT predictions and the Ames-296K values is minimized, the effective dipole used by SPCAT is the right one to compare with the dipole given by the empirical formula, Eq.(1). This procedure leads to μ with precision $1\text{E-}6 \sim 1\text{E-}7 D$.

The μ_{000} values are first determined for the 6 Ames-296K IR line lists. See Table 1 for comparison. The best agreement is found with the *av5dz* DMS, while the core-correlation effects at the QZ level raise the μ_{000} deviations by more than 100%.

This procedure is repeated for 13 vibrational states. All the dipole values are collectively shown in Fig.1a. Compared to Eq.1 values (solid black squares), the relative deviations are 0.20-0.37% for “Published” and “*avqdz*”, 0.06-0.25% for “*av5dz*”, 0.44-0.67% for “*acvqz*” and “*awcvqz*”, 0.12-0.30% for “*davqdz*”. These are always close to the $\delta\%$ of μ_{000} in Table 1. It is obvious the μ_{000} difference plays the primary role.

Setting all the μ_{000} as zero, the vibrational changes $\delta\mu = \mu_{v_1v_2v_3} - \mu_{000}$ are plotted in panel *b*. Compared to Eq.(1) (solid black squares), the vibrational dependence is similar for all 6 DMS fits. For any vibrational state shown in Fig.1b, the $\delta\mu$ are highly consistent. Inconsistencies are as small as $0.5 \sim 2.2\text{E-}4 D$. If we define $\Delta_\mu = 100\% \cdot (\delta\mu_{\text{Ames}} - \delta\mu_{\text{Eq.1}}) / \delta\mu_{\text{Eq.1}}$, the Δ_μ value for the 9 vibrational states excluding nv_1 ($n=1-3$) is in the range of $-1 \sim 10\%$. For v_1 to $3v_1$, Eq.1 predicts $\delta\mu = 1.4\text{E-}4 D$, $2.4\text{E-}4 D$, and $3.0\text{E-}4 D$. In our calculations, the corresponding $\delta\mu$ are $0.75\text{E-}3 D$, $1.47\text{E-}3 D$, and $2.41\text{E-}3 D$. The differences among the 6 DMS fits is only $\sim 6\%$ of $\delta\mu$. This nearly one-order of magnitude discrepancy relative to the other vibrational states is noted, but we have not been able to determine a reasonable explanation. We did verify the numerical procedure in Ref.[38]. The v_1 -related coefficients in Eq.1 appear normal. Either the original experimental results have a typo somewhere, or this vibrational mode requires a much more accurate PES to get its dipole right. Neither of the two possibilities can be verified very easily. Although we are preparing for the next version of our SO_2 PES refinement, nobody really knows if, or how far, the nv_1 and $\delta\mu(nv_1)$ can be further improved.

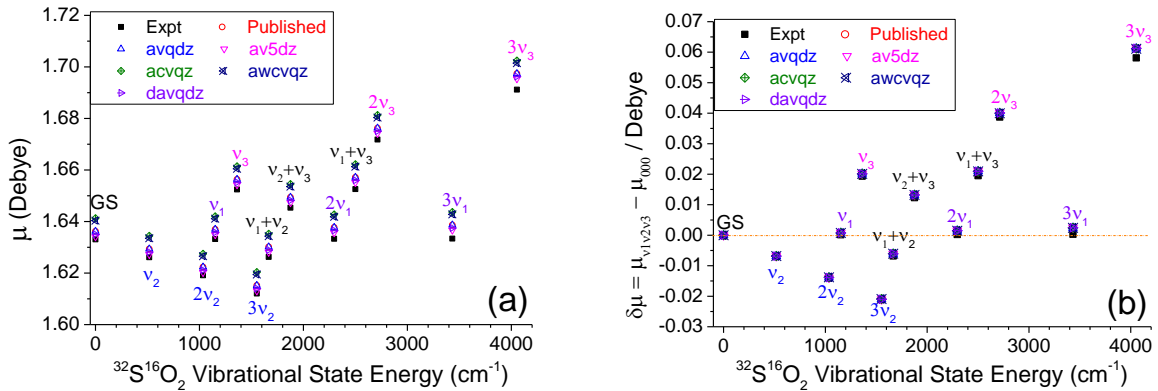


Fig.1 The effective dipoles (vibrationally averaged) of SO_2 vibrational states. Five new DMS fits are compared to empirical (Expt) values and original “Published” Ames DMS. (a) absolute value; (b) the vibrational dependence of dipoles, with respect to the $\mu_{000}(\text{GS})$ of each DMS or empirical formula.

Another possibility is the *ab initio* method and/or one-particle basis set. The only other alternative method for highly accurate DMS construction is icMRCI, i.e. the internally contracted Multi-Reference Configuration-Interaction method. As far as we know, its convergence is not faster, or slower, relative to that of CCSD(T) dipole calculations. Fig.2 presents the basis set effect on the dipoles of 13 vibrational states.

The “Published” and “*avqdz*” symbols essentially overlap with each other. This verifies that the “Published” DMS fit is numerically stable in the low energy region around the minimum. All the *Calc* – *Expt* deviations are > 0 . This indicates systematic deviations. The “*av5dz*” dipole deviations for the GS and the nv_2 states are only 1/3 of “*avqdz*” dipoles. This suggests the largest contributing factor is the incompleteness of the *ab initio* basis sets. The “*davqdz*” deviations are between “*av5dz*” and “*avqdz*”. This can be explained because “*davqdz*” is also between the QZ and 5Z levels. The extra diffuse function on the O atoms effectively increases the basis size. In the future we may add relativistic corrections and complete basis set limit extrapolations into the DMS. Currently, the core-correlation effects in “*acvqz*” and “*awcvqz*” shift all dipoles up by about 0.005 Debye. One may argue the small deviations of “*av5dz*” is the consequence of error cancellations, while the extra diffuse function on the S atom in (*d*)*avq/5dz* basis does not exist in the *a(w)cvqz* basis, either. When energies go higher, the deviations also increase. Such increases are not dependent on the one-particle basis sets. The colored groups of *Calc* – *Expt* symbols are parallel to each other. These increases are probably not the result of PES inaccuracy at higher energies. Use the data in Figs.1-2 and Table 1, interested readers may derive new empirical formula for the vibrational dependence $\delta\mu$.

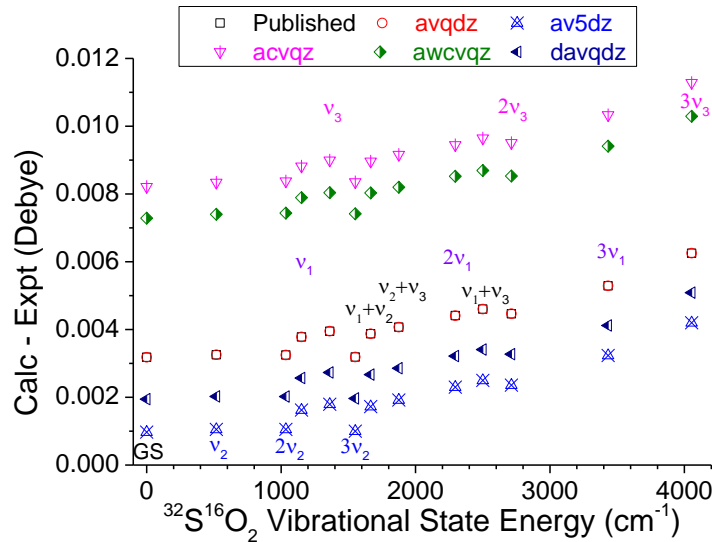


Fig.2 Agreement between the experimental model (Eq.1) dipoles and the effective dipoles we computed for 13 SO_2 vibrational states using 6 *ab initio* DMS. The empirical dipole values computed from Eq.1 are taken as zero. All Ames dipoles are relative values with respect to them, *Calc* – *Expt*. The basis set effects are obvious. See text for more discussion.

In short, the “Published” Ames DMS deviations are +0.20-0.40%. This may cause up to +0.4-0.8% deviations on transition dipole moments (TDM) and intensity. Examining the purely rotational microwave intensities of $\text{GS} \leftarrow \text{GS}$ or $v_2 \leftarrow v_2$, the Ames vs. HITRAN/CDMS intensity agreement near $J/K_a=0$ are

within 1%.[42] However, if we look at the higher J/K_a or the Table 3 of Ref.[42], many bands have intensity deviations $\pm 10\text{-}20\%$. Therefore, it is safe to conclude that, these $<0.5\%$ DMS defects are *not* the major cause of IR intensity discrepancy. The main factor should be the uncertainties in the experimental measurements and isotopologue inconsistency of EDM models. An example is given in Section 6.

The isotopologue variance of μ_{000} and $\delta\mu$ is an interesting extension to study in the future. However, there does not exist Stark effect measurements for μ_{000} and $\delta\mu$ of minor isotopologues. The accuracy of experimentally measured IR and microwave intensities is *not* high enough to disprove theoretical predictions.

3. SO₂ Partition Sum: convergence along J and wavenumber

We re-ran $J=0\text{-}150$ calculations to check the partition sum convergence of the published Ames-296K IR lists, which were based on $J=0\text{-}75$ VTET calculations. The energy cutoff for rovibrational levels is set to 0.045 Hartree – zero-point energy, or 8347 cm⁻¹. At 296K and 750K, the partition sum is 6337.129 and 45159.11.

Fig.3a-b plots the J convergence at 296K and 750K. It uses relative weights since they can easily be converted to absolute partition contributions. Panel *a* uses a regular scale, while panel *b* uses log10 scale. Three series of weights are shown related to total partition sum Q_{total} : red circles for $q(J)$, i.e. the contribution from each J ; black triangles for $Q(J)=\sum_0^J q(J)$, i.e. the partition sum accumulated from 0 to J ; blue squares for the missing part, i.e. $Q_{\text{Total}}-Q(J)$.

At 296K, the missing part associated with J cutoff at 75 is only $2\text{E-}4$, or 0.02%. This defect is much smaller than the uncertainties in experimental IR measurements and EDM analysis, theoretical DMS convergence defects, or even the PES accuracy defect. Recently we reported two very similar CO₂ PES may cause $>0.5\%$ discrepancy in the 30013-00001 band intensity.[43] At 750K, the defect has risen to 3.5%. We need J up to 120 before the $Q(J)$ defect reaches $2\text{E-}4$. Thus a scaling factor is recommended for higher temperature intensity conversions, e.g. for simulations using Venus atmospheric parameters.

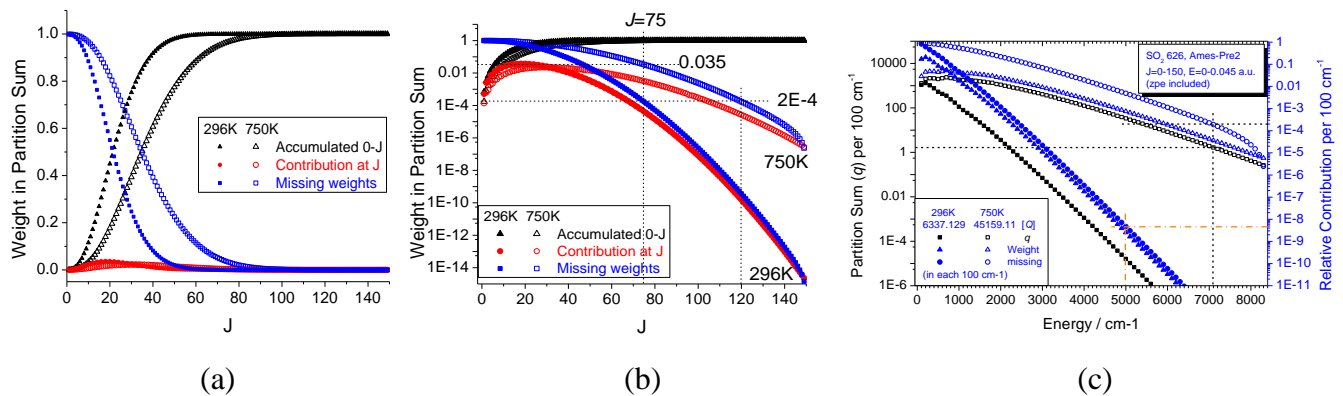


Fig.3 (a-b) Single J contribution, accumulated 0- J contribution, and the missing part of SO₂ 626 partition sum, divided by Q_{Total} at 296K or 750K. $J=0\text{-}150$ calculations were carried out on Ames-Pre2 PES, eigenvalues are cutoff at 8347 cm⁻¹ above the ZPE. (c) Left: Partition contribution from energy levels in each 100 cm⁻¹ (black squares); Right: relative weight for every 100 cm⁻¹ contribution (blue triangles); and the Q_{Total} defect, “missing” weight (blue circles). Solid symbols for 296K, open symbols for 750K.

Convergence along the E cutoff is given in Fig.3c. The statistics are for every 100 cm^{-1} , from 0 to 8300 cm^{-1} . At 296K, SO_2 626 levels up to 5000 cm^{-1} (above ZPE) have a Q defect less than $1\text{E-}8$. Therefore, the quality of the previously published Ames-296K intensities are not affected by E cutoff at 8000 cm^{-1} (but are still affected by the J cutoff). At 750K, we need $>7100 \text{ cm}^{-1}$ to converge better than 99.98%, i.e. a defect $< 2\text{E-}4$.

4. EH model consistency and parameter ranges

Since the Ames-296K IR intensities are to be combined with more energy levels (and transition line positions) derived from EH models, it is necessary to understand the accuracy and consistency of the best EH models we can find for SO_2 isotopologues. This is a critical step for the quality control of our IR list product. Here we discuss the reliability and quality of EH high order parameters and potential improvements.

In Ref.[23], Perrin and co-workers pointed out the sextic EH parameters H_{JK} and h_{JK} could not be determined from the 628 & 828 least-squares fit due to the correlations with other EH parameters. Such observations are common to other isotopologues. For example, some higher order terms of 636/646/627/628 in CDMS were fixed at the main isotopologue (626) values,[44] and further used in recent EH models.[21] In reality, no standard rule was ever developed to determine which higher order EH parameters should, *or should not*, be fixed or set to zero. Obtaining a good least-squares fit is the primary concern, and the fitting difficulty for a specific EH parameter may vary from one isotopologue to another, and maybe from one group to another. Taking h_{JK} as an example, CDMS fixed the h_{JK} of 636 and 628 at its 626 value -4.28 mHz.[45] The LISA EH model [23] also fixed the 628 h_{JK} at a CDMS 626 value, but it is a different h_{JK} , -6.97 mHz. It was taken from another CDMS EH model.[46] We understand that this will not have a noticeable effect on the present work, it just shows that EH models are not fully consistent across isotopologues.

Scientists sometimes argue there is no “true” high-order EH constants. From our experience, this claim is not 100% valid for all high-order EH constants. The theoretical Ames-296K IR lists are computed in a consistent manner. Hence these may provide a valuable reference on the isotopologue consistency of EH parameters. Our recent “Ames list + EH model” study on the vibrational ground state of SO_2 isotopologues [31] confirms that the h_{JK} values are in the range from -7 mHz to 2 mHz, which seem difficult to predict from one isotopologue to another. But stable ranges do exist for most higher order EH parameters. Fitting the 30 Ames-296K lists to the same EH model (all parameters are uniformly weighted), we find the sextic terms in the following ranges: $H_{JK} = 20\text{-}35 \text{ mHz}$, $H_J = 8\text{-}12 \text{ mHz}$, $h_J = 3.5\text{-}6 \text{ mHz}$. The ranges for octic constants are: $-L_J = 2\text{-}4\text{E-}8 \text{ Hz}$, $-L_{JJ} = 1\text{-}2\text{E-}6 \text{ Hz}$, $L_{JK} = 1\text{-}4\text{E-}5 \text{ Hz}$, $L_{JJK} = 2.5\text{-}4.5 \text{ mHz}$, and $-L_K = 50\text{-}80 \text{ mHz}$, $-l_J = 1\text{-}2\text{E-}8 \text{ Hz}$, $l_{JK} = 0.2\text{-}1.0\text{E-}6 \text{ Hz}$. The ranges for the decic parameters are: $P_{KKJ} = 0.5\text{-}1.2\text{E-}8 \text{ Hz}$, and $-P_{KKKJ} = 0.5\text{-}1.0\text{E-}6 \text{ Hz}$. It is interesting to see the octic and decic terms stay in a well confined range while h_{JK} oscillates between negative and positive values in a range larger by 2-5 orders of magnitude, i.e. a few mHz vs. $1\text{E-}8\text{-}1\text{E-}5 \text{ Hz}$. Note that we are not claiming these ranges are “accurate”, but most of them are systematic, reliable, and probably predictable from one isotopologue to another. The “Ames list + EH model” paper[31] includes a performance check on the prediction formula Ulenikov et al.[19] adopted in their 828 EH models.

5. Intensity Consistency: Ames vs Expt.

In 2017, we demonstrated that the variationally computed intensities are highly consistent among CO₂ isotopologues.[43] The consistency is usually higher than that of experimental EH models by at least 1-2 orders of magnitude. A recent quantitative check on SO₂ microwave (MW) and IR transitions actually confirmed the consistency may be better than 99.9%.[31] Such consistency is more than capable of providing a sanity check on experimental intensities and EDM models, at least for the low energy vibrational bands of a molecule like SO₂.

In Fig.4a, the transition dipole moments (TDM, or $\langle|\mu| \rangle^2$) of transitions taken from the GS rotational band and 3 combination bands are plotted vs. the composite isotope mass coordinate defined as the sum of the inverse of atomic masses, where $m_O=16/17/18$ and $m_S=32-36$. Two different transitions are selected because their vibrational band symmetries are different. For convenience, the relative ratio $TDM_{ISO}/TDM(626)$ is plotted, instead of the original TDM quantities. With accurately computed partition sums, population, and transition wavenumbers, the consistent TDMs in Fig.4a directly link to the high consistency of the Ames-296K line list intensities. Given 2-3 isotopologue intensities, one can reliably predict the TDMs and intensities of all other isotopologues. This is the predictive power of the “Best Theory + Reliable High-resolution Experiment” (BTRHE) strategy. The 0.01-0.02 cm⁻¹ accuracy on rovibrational energy levels and transitions energies are the guarantees on wavefunctions, partition functions, and populations.

All TDM changes are systematic on isotopic substitution. The pure rotational transition $13_{13,1} \leftarrow 12_{12,0}$ has a very stable TDM, with changes less than 0.3% across the 30 isotopologues. The O and S isotope effects on the other 3 TDMs are nearly linear, in the range of ± 10 -40%. Heavier S and O isotopes will raise the TDM (and intensity) of the 110 ($\nu_1+\nu_2$) and 011 ($\nu_2+\nu_3$) bands, but reduce the TDM (and intensity) of the 101 band. The intensity (S) order for the 110 and 011 bands is $646 > 626 > 828 > 628$, while the TDM order is $646 > 626 > 628 > 828$. The intensity of 628 is lower than 828, because the partition sum $Q(628)$ is nearly double the $Q(828)$ value.

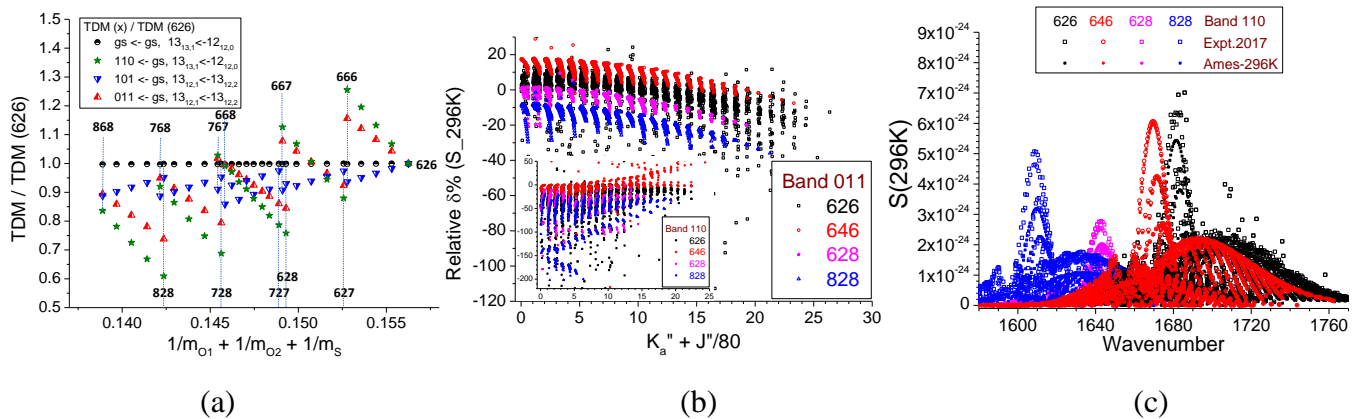


Fig.4 (a) Isotopologue consistency of Ames Transition Dipole Moments (TDM) for pure rotational band and 3 combinational bands, the values are divided by the TDM of main isotopologue (626); (b) the $\nu_2+\nu_3$ (011) band intensity agreements between Ames vs. Expt.[12], compare to those $\delta\%$ of $\nu_1+\nu_2$ (110) band in the in-set panel; (c) the $\nu_1+\nu_2$ (110) band intensity of Ames (solid dots) and Expt.(open squares).[12]

In 2017 Ulenikov *et al* [12] reported $\nu_1+\nu_2$ (110) and $\nu_2+\nu_3$ (011) band intensities for the 4 isotopologues to which they have made great contributions, 626/646/628/828. Intensities are compared in Figs.4b and 4c. The relative difference is defined as $\delta\% = 50\%(S_{\text{Ames}}/S_{\text{Expt}} - S_{\text{Expt}}/S_{\text{Ames}})$. In Fig.4b, most $\delta\%(011)$ fall within $\pm 20\%$. Similar to the $\delta\%$ of CO_2 isotopologue EDMs,[43] such agreement is reasonable and fully within our expectations. 5-15% uncertainty is normal for the experimentally fitted EDM terms. All 4 EDM models show similar K_a and J dependence. The $\delta(628)$ distribution is between $\delta(626)$ and $\delta(828)$. These EDM models seem roughly consistent among the 4 SO_2 isotopologues, but their EDM term uncertainties are large enough to cause the observed $\delta\%$ range.

On the other hand, the $\delta\%(110)$ is shown as an insert to Fig.4b, where the $\delta = -150\% \sim -50\%$ indicates the $S(\text{Ames})$ of 628 and 828 are much lower than the $S(\text{Expt})$ reported in Ref.[12] as calculated from the fitted EDM models. Only the agreement for 646 looks fine. Agreement for 628 and 828 is far worse than the 011 band. Since the $S(\text{Ames})$ are isotopologue consistent, it is concluded the experimental EDM models are not consistent. From the strong J -dependence of δ , certain J related terms in the 626/628/828 models require fixes. A branch of $\delta(828)$ also shows clear K_a dependence, suggesting a $K_{a/c}$ related issue as well.

Instead of δ , Fig.4c directly plots 4 isotopologue intensities. Experimental and Ames intensities show excellent agreement around the 646 (red circles and dots) peak at 1670 cm^{-1} . Agreement looks acceptable for the 626 peak at 1682 cm^{-1} , but it effectively causes the experimental $S(626) > S(646)$. This contradicts with the $S(646) > S(626)$ rule revealed in Fig.4b. Furthermore, the experimental peak intensity ratio $S(626)/S(828)$ is about 1.2, much smaller than the Ames ratio ~ 1.85 . Therefore the experimental 828 intensity was significantly overestimated. If experimentalists know the approximate intensity ratio across these isotopologues, the most possible source for such $\delta\%$ inconsistency is the uncertainty of isotopologue abundances estimated in the laboratory experiments.

In 2018, an extended IR analysis was published for the 626 ν_2 band,[47] with new intensity values and EDM terms. Compared to the Ames-296K lists (old and new), the relative $\delta\%$ has K_a and J dependences similar as before.[25,26] However, near $J/K_a=0$, $\delta=17\%$. This seems too large, inconsistent with the 0-2% deviations we found for other bands and isotopologues in the existing HITRAN data.[25,26] It is also inconsistent with the DMS quality check we reported in Sec.2. Based on our knowledge and experience, the quantum exact rovibrational calculations (within the Born-Oppenheimer approximation frame) we carried out on the spectroscopically accurate, empirically refined Ames-Pre2 PES using a precisely fitted CCSD(T)/aug-cc-pV(Q+d)Z dipole surface are expected to achieve (at least) better than 95% agreement (i.e. $\delta < 5\%$) for low J/K line intensities of such low energy vibrational fundamental bands of such a tightly bounded, closed shell, triatomic molecule. Examining Fig.4b, the $\delta(\nu_2+\nu_3)$ and $\delta(\nu_1+\nu_2)$ near $J/K_a=0$ are also in a range as large as $\pm 10\text{-}20\%$. The intensity of the Ames IR lists and previous EDM models should be more reliable, at least before third-party IR analysis finds consistent $\delta(\nu_2)$ for other isotopologues.

6. Three IR Line List Sets: New Lines \rightarrow Expanded \rightarrow Ames+MARVEL

Details of the Ames PES refinement, dipole moment surface (DMS), and IR line list calculations can be found in Refs.[25,26], so they are not repeated here. Given an intensity cutoff of $1\text{E-}30\text{ cm/molecule}$ and $E' < 8000\text{ cm}^{-1}$ above the zero point, the Ames-296K lists have 4.1-4.6 million lines for the symmetric

isotopologues 626,636,646 and 828, and 10.4 millions lines for 628. Combining these Ames-296K line lists with new experimental data after 2009, HITRAN based levels, and the recent MARVEL list[48], we have generated 3 sets of IR lists:

- (1) New Lines Set – match experimental line positions and rotational-vibrational quanta to Ames lines
- (2) Expanded Set – match Expt./HITRAN Effective Hamiltonian (EH) model levels to Ames lines
- (3) Ames + MARVEL Set – match MARVEL levels to Ames lines.

Why 3 sets? Because we cannot find experimental line positions for 636 bands, and the MARVEL analysis was done on 626/636/646 only. There are 4 lists in the New Lines Set for 626/646/628/828; 5 lists in the Expanded Set for 626/646/636/628/828; and 3 lists in the Ames+MARVEL set, for 626/636/646. The latter two sets have the cutoff $1\text{E-}26$ cm/molecule to limit data size and maintain data purity.

The procedure matching the New Lines Set is designed to identify and filter out the typos and misassignments in the experimental data. It requires

- (1) rotational quantum number J'/J'' agree (for 628, all K_a/K_c must agree);
- (2) line position, upper/lower state energy E'/E'' , all agree within ± 0.1 cm^{-1} ;
- (3) checking the stability of the Ames intensity.

Each transition of the New Lines Set is noted by the experimental reference. Note the typos and misassignments are not the focus of this work, as long as the final IR lists are reliable.

The “match” for the Expanded and Ames+MARVEL sets just means that we extract all Ames-296K lines with accurate E'/E'' levels available from experiments, EH models, HITRAN data or MARVEL analysis, and replace the corresponding E'' and line position.

For the 626 and 646 data in HITRAN, we only use those levels derived from transitions carrying the line position uncertainty index $ierr \geq 4$, which means accuracy better than 0.0001 cm^{-1} . These are the energy levels included in the Ames-1 and Ames-Pre2 PES refinements. However, some important bands have $ierr=0$, e.g. the $\nu_1+\nu_3$ band at ~ 2500 cm^{-1} and $3\nu_3$ band at ~ 4000 cm^{-1} . Some other bands were reported but not in HITRAN2008-2016, e.g. the $2\nu_1$ band ~ 2300 cm^{-1} . [49].

In the “Expanded Line Set” construction, the following EH models were adopted for the vibrational ground states: the 2013 Tomsk model [16] for 626, the CDMS (Cologne Database for Molecular Spectroscopy) [50–52] model for 646 [44], the LISA models for 636 [21,22] and for 628 and 828 [23]. These models are combined with the “New Line Sets” and HITRAN levels (626 & 646) to generate the empirical E'/E'' and line positions.

The most recent MARVEL[53,54] study [48] collected SO_2 lines from 43 experimental sources since 1951, and generated a trusted set of 15,130 / 10,893 / 5852 empirical levels for 626 / 646 / 636, respectively. The energy levels were labeled by 6 quality grades. From our point of view, a major advantage of MARVEL lists comes from the consistency check with EH models having reached $\sigma_{\text{RMS}} = 1\sim 4\text{E-}4$ cm^{-1} , while the superiority and extrapolation reliability of EH models unavoidably depend on the input levels of a specific isotopologue / band, which finally trace back to the laborious efforts in IR experiments. But our goal is to provide high quality IR intensities for reliable 626, 646, 636, 628 and 828 lines reported

after HITRAN2008. With such differences in goals, data ranges, approaches, and the criteria identifying/fixing “bad data”, it is beyond the scope of this paper to run detailed comparisons. But the Ames+MARVEL IR lists can provide valuable references for 626, 636 and 646 IR analysis.

As shown in Table 2, in the 626 “Expanded Line Set”, 161,373 of 195,425 lines are able to match the E'/E'' counterparts in the MARVEL lists. The Δ s of line position, E' and E'' are computed and added to the end of each transition line. Other lines are marked by ‘-’ in the supplementary data file. In total, 58% / 93% / 97% of the 161,373 lines position Δ s are within 0.0001 / 0.0005 / 0.0010 cm^{-1} . Only 122 line positions have $|\Delta| > 0.01 \text{ cm}^{-1}$, and $|\Delta|_{\text{max}} = 0.024\text{-}0.045 \text{ cm}^{-1}$. The outliers mainly involve $3\nu_2$ levels or high $K_a \nu_1$ levels. The $|\Delta|_{\text{max}}$ for 636 and 646 are 0.0026 and 0.0030 cm^{-1} , respectively. The % of $|\Delta| < 0.0001 / 0.0005 / 0.0010 \text{ cm}^{-1}$ are different for each isotopologue, which indicates the subtle EH model differences between MARVEL and the previous Expt/HITRAN/CDMS data.

The “Ames+MARVEL” Line Sets are generated with $1\text{E-}26 \text{ cm/molecule}$ cutoff. The 626/636/646 sets have 195,882 / 79,927 / 159,729 lines, respectively. The size of 626 and 646 lists are close to the “Expanded Line Sets”, but 636 lists are less by 33% because the 636 Expanded Set construction used rovibrational levels with much higher J/K_a , 99/35 vs. 78/23. As expected, most Δ (Ames – MARVEL) deviations are within $\pm 0.03 \text{ cm}^{-1}$. Exceptions include $3\nu_2$ related 626 lines, $3\nu_1$ related 646 lines, and some $J > 55$ lines of 636 and 646.

Table 2 gives a summary for the three sets of IR lists. From our experience in data reliability and the requirements for room-temperature IR simulations, we recommend a $J'' \leq 50$ and $K_a'' \leq 25$ restraint for the most reliable Ames-296K intensity. The lists are plotted in Fig.5 and discussed in next section

Table 2. Transition statistics for the New line sets of 626/646/628/828, Expanded line sets of 626/636/646/628/828, and Ames+MARVEL line sets of 626/636/646.

Iso	626	646	828	628	636
New Line Set					
#Lines Collected	29,265	28,684	12,941	21,317	
#Lines Matched	28,254	28,073	12,837	20,865	
with 1E-26 cutoff	26,464	25,089	12,453	20,820	
cm^{-1} range	991-4059	428-3465	1016-2684	1046-2710	
$J''_{\text{max}} / K''_{\text{max}}$	75/37	75/29	75/25	75/25	
Expanded Line Set					
#Lines (1E-26)	195,425	162,403	118,563	242,889	123,431
cm^{-1} range	0-4151	0-3465	0-2921	0-2974	0-2625
$J''_{\text{max}} / K''_{\text{max}}$	75/42	75/39	75/34	75/32	75/35
# ($J''/K_a'' < 50/25$)	157,468	144,551	100,377	212,192	80,154
MARVEL Check	161,373	153,515			79,927
$ \Delta < 1\text{E-}4, 5\text{E-}4, 1\text{E-}3 \text{ cm}^{-1}$	58%/93%/97%	28%/67%/92%			57%/98%/99.7%
$ \Delta _{\text{max}}$	0.0447	0.0030			0.0026
Ames+MARVEL Line Set					
(618,834)*		(454,581)*			(175,229)*
#Lines (1E-26)	195,882	159,729			79,927
$J''_{\text{max}} / K''_{\text{max}}$	75/35	75/29			75/22
# ($J''/K_a'' < 50/25$)	170,816	147,687			69,651
Partition Sum (296K)	6333.93	6459.67	7400.24	13674.02	6398.13
#Lines in HITRAN	72,460	22,661			

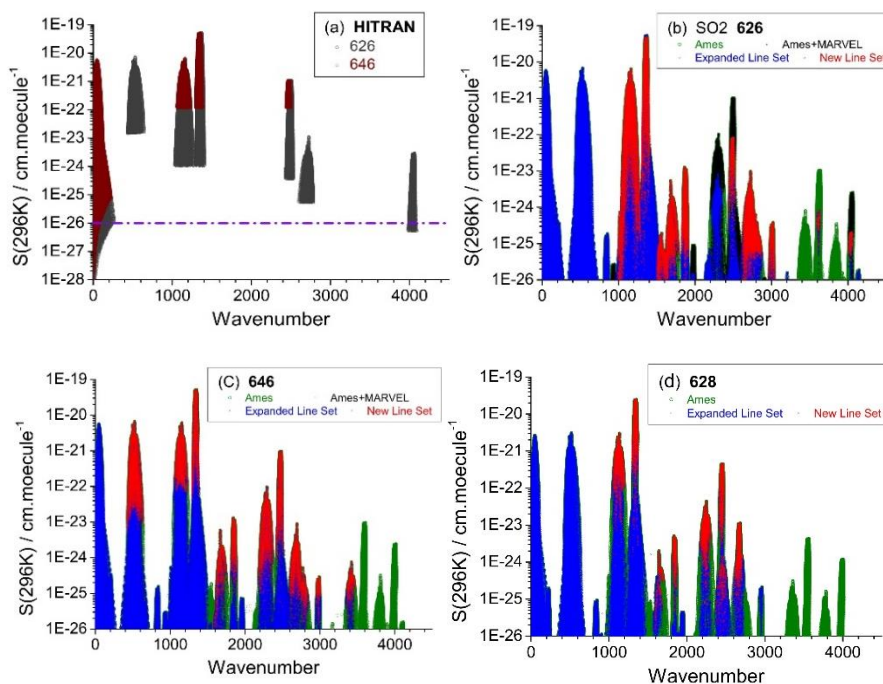
* the number of lines having Ames-296K intensity $> 1\text{E-}30 \text{ cm/molecule}$.

7. Coverage Improvement, Missing bands, and the Best Choice

Now comes the question: which IR lists should we trust or use? For 626/636/646, if we are confident with all MARVEL levels, a safer choice would be the $J \leq 50$, $K_a \leq 25$ subset of the “Ames+MARVEL” lists, supplemented by (if there are any) other transitions in the “Expanded Line Sets”. For 628 and 828, the safer choice is the $J \leq 50$, $K_a \leq 25$ subset of the “Expanded Line Sets”. Considering that the need for coverage expansion is more urgent than the accuracy for each transition, it is probably more appropriate to build an inclusive, composite list having all lines discussed in this paper included. Quality control may assign lower grades to high J/K_a lines, non-MARVEL levels, or from different line sets. This recommendation arises from Fig.5.

Fig.5a shows the current HITRAN[24] SO₂ data. There are only 72,460 (22,661) lines or 7 (4) discrete segments for 626 (646), including 24,119 (11,896) purely rotational lines. Excluding rotational lines < 350 cm⁻¹, most 626 line intensities > 1E-26~1E-23 cm/molecule, and 646 line intensities > 1E-22 cm/molecule. Therefore we chose 1E-26 cm/molecule to be the intensity cutoff. This choice eliminates the 7-11% weakest lines of 626 and 646, and 2-3% of the lines of 628 and 828, as shown in Table 2.

Figs.5b-f compares the three sets of line lists plus the Ames-296K list for the 5 isotopologues. Red, blue, black, and green represent the New Lines, Expanded, Ames+MARVEL, and Ames lists coverage, respectively. Please remember all intensities are plotted in 100% abundances, i.e. not scaled by terrestrial abundances. Compared to HITRAN data in Fig.5a, the improvements are significant, but each isotopologue still has a lot of gaps to fill in the 0 – 4200 cm⁻¹ range. All isotopologues are completely blank above 4200 cm⁻¹. The green area associated with the Ames lists indicate the vibrational bands missing from high-resolution experimental IR studies.



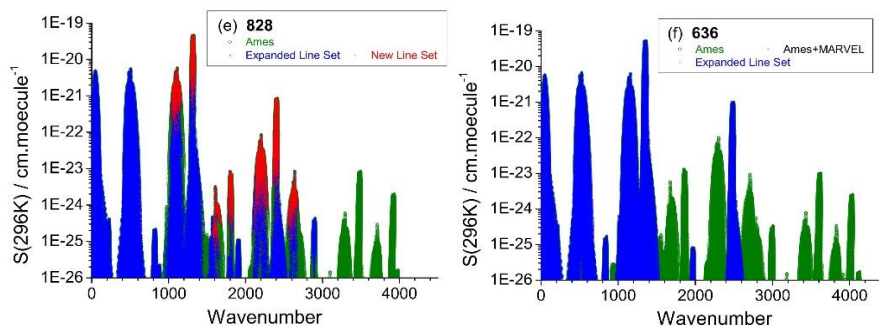


Fig.5 Data coverage of HITRAN (a), the New Line sets (b-e, red dots), the Expanded line sets (b-f, blue dots), the Ames+MARVEL line sets (b,c,f, black dots, shadowed by blue dots). The green dots (Ames-296K intensity, $J''/K_a'' \leq 50/25$) not covered by other line sets indicate the missing bands below 4500 cm^{-1} .

From Fig.5c to Fig.5f, a common observation on the data coverage is that $\text{red} \in \text{blue} \cong \text{black} \in \text{green}$. But in Fig.5b, several places appear black, i.e. $\text{blue} \in \text{black}$. This means some important vibrational states can be found in the MARVEL 626 level list, but not in the HITRAN level list – which we used for Expanded List set construction. As we pointed out earlier, transitions involving those states either had line position uncertainty index $ierr < 4$, e.g. $\nu_1 + \nu_3$ ($\sim 2500 \text{ cm}^{-1}$) and $3\nu_3$ ($\sim 4000 \text{ cm}^{-1}$), or are not included in HITRAN, e.g. the $2\nu_1$ band $\sim 2300 \text{ cm}^{-1}$. [49] Consequently, the hot-bands $\nu_1 + \nu_3 \leftarrow \nu_2$ ($\sim 2000 \text{ cm}^{-1}$) and $2\nu_1 \leftarrow \nu_3$ ($\sim 930 \text{ cm}^{-1}$) are also missing from the Expanded Line Set. In addition, the strong feature at 3600 cm^{-1} belongs to $2\nu_1 + \nu_3$, but all of our 3 new sets only have its hot-band $2\nu_1 + \nu_2 + \nu_3 \leftarrow \nu_2$. [13] Both Ref.[55] in 1996 and Ref.[13] in 2010 published their EH models fitted from observed line positions, but not the original line positions. It is not in HITRAN, either. Consequently, no $2\nu_1 + \nu_3$ levels ever appeared in our analysis / comparisons, and these are not in the MARVEL lists either. Although we do not know why the $2\nu_1 + \nu_3$ transitions were not collected in HITRAN, it is one of the last missing blocks in the $0 - 4200 \text{ cm}^{-1}$ range. The other two missing blocks are $3\nu_1$ and $\nu_1 + 2\nu_3$. Their total band intensities ($\times 10^{20}$) are 0.0373, 0.541, 0.0124 and $1.326 \text{ cm/molecule}$, for $3\nu_1$, $2\nu_1 + \nu_3$, $\nu_1 + 2\nu_3$, and $3\nu_3$, respectively. The Expanded Line Sets and the next updates can definitely benefit from these valuable EH models.

In the mean time, we may also need transition data for other important minor isotopologues. According to our abundance estimates, ~ 20 isotopologues are needed to make the $1000\text{-}1500 \text{ cm}^{-1}$ range really “complete” down to $1\text{E-}30 \text{ cm/molecule}$. Even with $1\text{E-}26 \text{ cm/molecule}$ cut-off, we need the 11 most abundant isotopologues, which include 627 / 666 / 648 / 647 / 638 / 637, and the 5 isotopologues in Fig.5.

8. Conclusion

The quality of the previously published Ames SO_2 dipole moment surface is investigated. The dipole moments of $^{32}\text{S}^{16}\text{O}_2$ vibrational states up to $3\nu_1$ computed on the refined Ames-Pre2 PES and DMS agree with the values predicted by an empirical formula (Eq.1) based on a 1979 Stark effect experiment. Relative deviations are 0.20~0.40%. New dipole surfaces have been constructed to test the *ab initio* basis set effects on the DMS, including $\text{QZ} \rightarrow 5\text{Z}$, core-correlation, and double augmentation. The tests confirm the numerical stability of our published DMS, at least in the low energy region around the PES minimum. The vibrational dependences $\delta\mu_{\nu_1\nu_2\nu_3} = \mu_{\nu_1\nu_2\nu_3} - \mu_{000}$ are highly consistent among all 6 DMS fits. See Fig.2.

The Ames $\delta\mu$ match the empirical $\delta\mu$ to better than 90%, except nv_1 states ($n=1-3$). The $\delta\mu$ discrepancy on nv_1 calls for more theoretical or experimental efforts. From “*avqdz*” to “*av5dz*”, the *Calc* - *Expt* deviations of the ground state and nv_2 ($n=1-3$) are reduced from 0.003 *D* to 0.001 *D*. The “*acvqz*” and “*awcvqz*” DMS including core-correlation effects raise the deviations by 0.005 *D*. See Fig.3. The convergence of the SO₂ 626 partition sum $Q(T)$ is checked at $T=296K$ and $T=750K$, vs. J_{\max} and E . Compared to Q_{296K} converged up to $J=150$, a 2E-4 or 0.02% is missing from the Q_{296K} estimated from $J=0-75$ rovibrational levels. E cutoff at 8000 cm⁻¹ does not affect convergence at 296K. At 750K, we need $J=120$ and $E \geq 7100$ cm⁻¹ to reduce the $Q(750K)$ defects below 2E-4.

With both the DMS and partition sum quantitatively validated, the Ames-296K IR intensities are combined with experimental line positions, EH models, and MARVEL levels to generate reliable IR lists for the SO₂ isotopologues 626, 636, 646, 628 and 828. Most experimental lines have been successfully matched. The Ames intensities are highly consistent for computations of the 30 isotopologues of ³²⁻³⁶S and ¹⁶⁻¹⁸O. The data products, including the “New Line Sets” (4 isotopologues), “Expanded Line Sets” (5 isotopologues), and “Ames + MARVEL” Line sets (3 isotopologues), are expected to be accurate and consistent enough for future HITRAN updates, and serving as valuable alternatives for IR analysis and simulations. These Line sets data can be downloaded from the supplementary file of this paper, or from the Ames Molecular Spectroscopic Database at <http://huang.seti.org>. Line position agreement is not explicitly discussed in this paper, but all the differences are also available in the supplementary line list files.

Fig.4b and 4c provide an example of how much the isotopologue EDM intensity model consistency may vary from band to band, and from one isotopologue to another isotopologue. For example, the *calc* - *expt* $\delta(646)$ are reasonable for both the 110 and 011 bands, in contrast with the other 4 isotopologues. Currently, the deviations of partition function and lower state energy can be easily reduced to less than 0.1% or even 0.01%, so the original measurement is probably the main source of observed discrepancy. This may result from the extra difficulty associated with isotope abundance determinations. Since the consistent theoretical IR lists are available for all SO₂ isotopologues, we suggest using them to check and improve the isotopologue consistency of experimentally fitted EDM models, especially the models of those relatively abundant isotopologues. In the future, if $\delta\%$ are highly consistent across isotopologues, the EDM intensities can be taken as a valuable guide to improve the accuracy of our dipole surface and theoretical IR intensities. Thus, this is a mutually beneficial interaction between experimentalists and theoreticians.

The next step for SO₂ high-resolution IR database enrichment may have contributions from several aspects. New lab measurements lead to new bands, new empirical levels and new line sets. High resolution IR spectra recorded in the 5000-8000 cm⁻¹ range will greatly boost our PES refinement and the predictive power of the Ames-296K lists. Highly sensitive measurements for the weak lines in spectral windows are important for the accuracy of high-temperature IR simulations. The hyperfine splitting of 636 and 627 lines may also be added. In addition, 627/666/648/848 band measurements may help refine our predictions for other less abundant isotopologues. The prediction accuracy of isotopologue MW spectra has been improved by two orders of magnitude using a new implementation of the BTRHE strategy,[31] whose product – a complete MW line set – may be incorporated as the best predictions available for the minor isotopologues.

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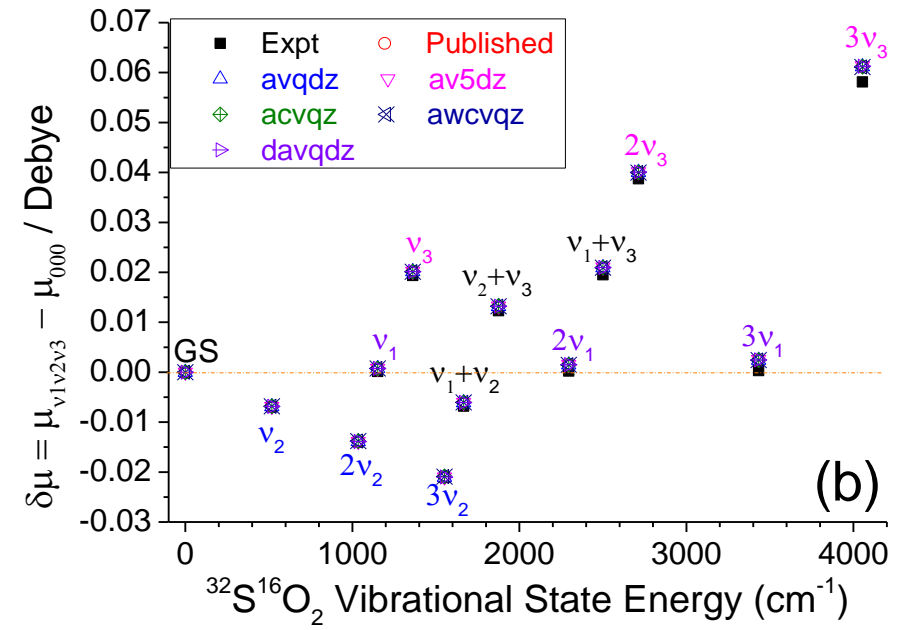
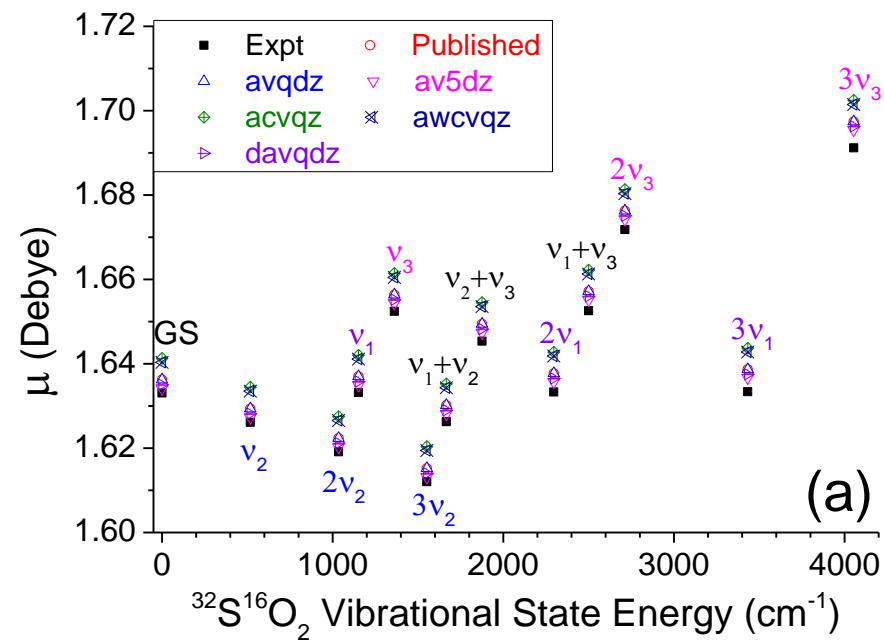


Fig.1 The effective dipoles (vibrationally averaged) of SO_2 vibrational states. Five new DMS fits are compared to empirical (Expt) values and original “Published” Ames DMS. (a) absolute value; (b) the vibrational dependence of dipoles, with respect to the $\mu_{000}(\text{GS})$ of each DMS or empirical formula.

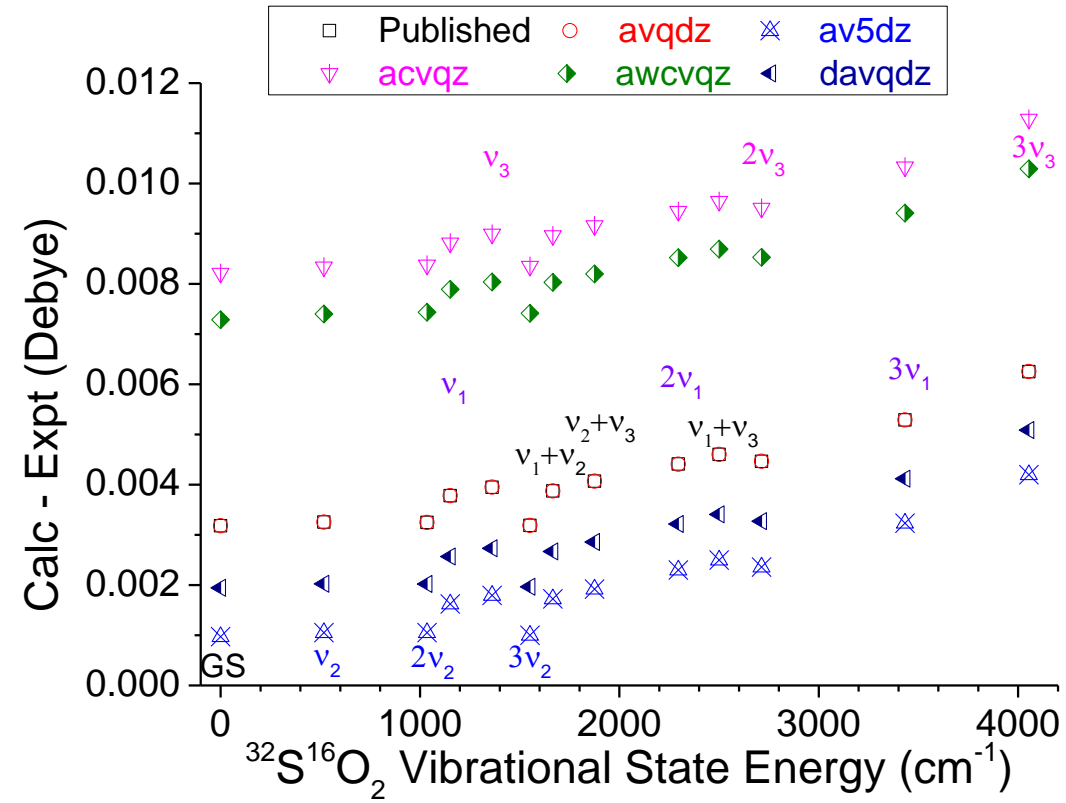


Fig.2 Agreement between the experimental model (Eq.1) dipoles and the effective dipoles we computed for 13 SO₂ vibrational states using 6 *ab initio* DMS. The empirical dipole values computed from Eq.1 are taken as zero. All Ames dipoles are relative values with respect to them, Calc - Expt. The basis set effects are obvious. See text for more discussion.

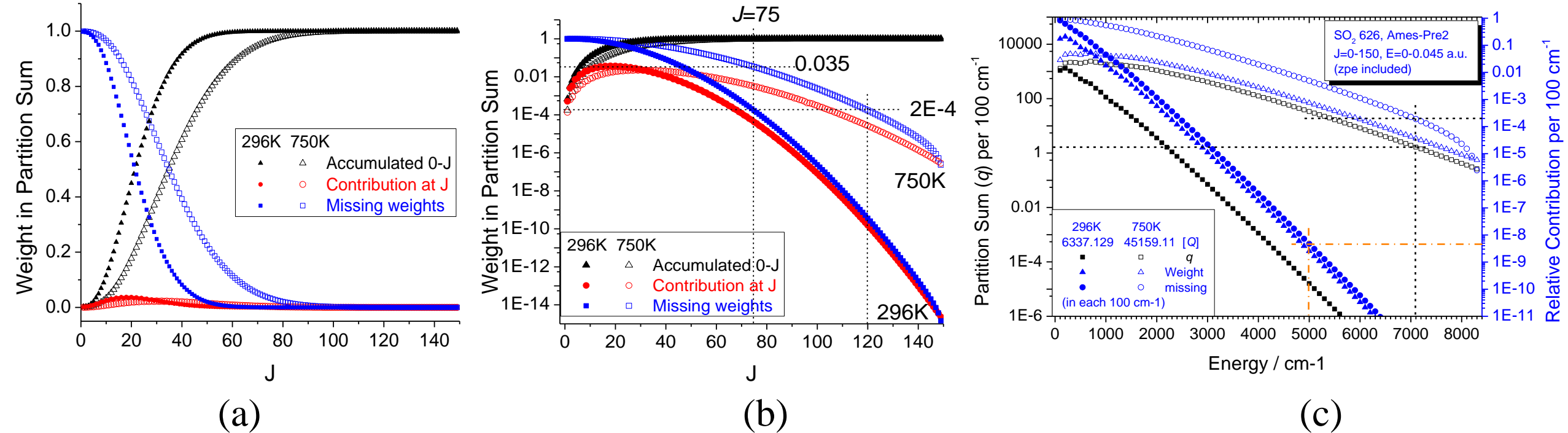
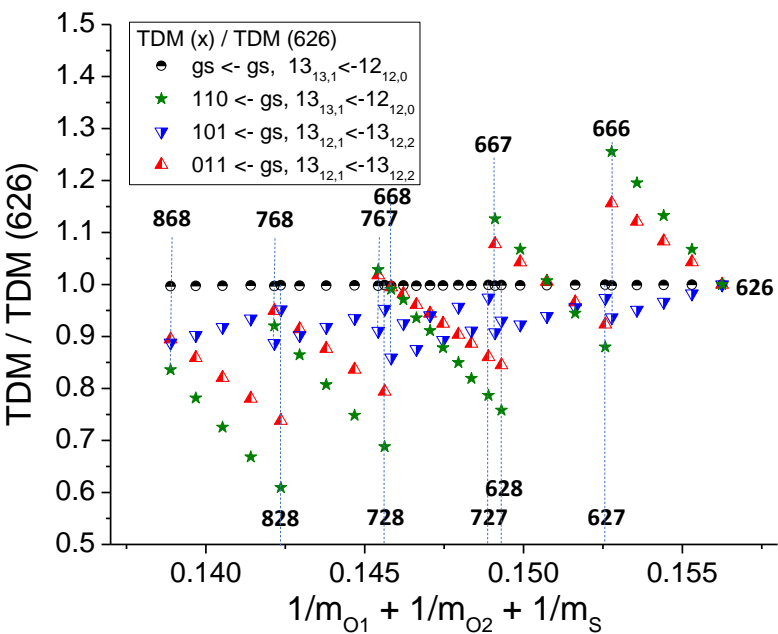
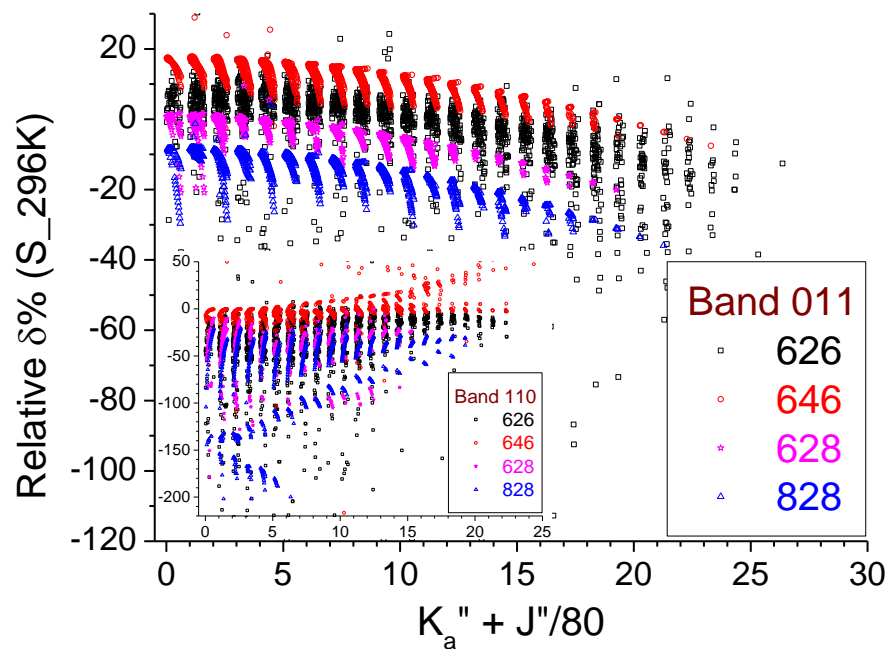


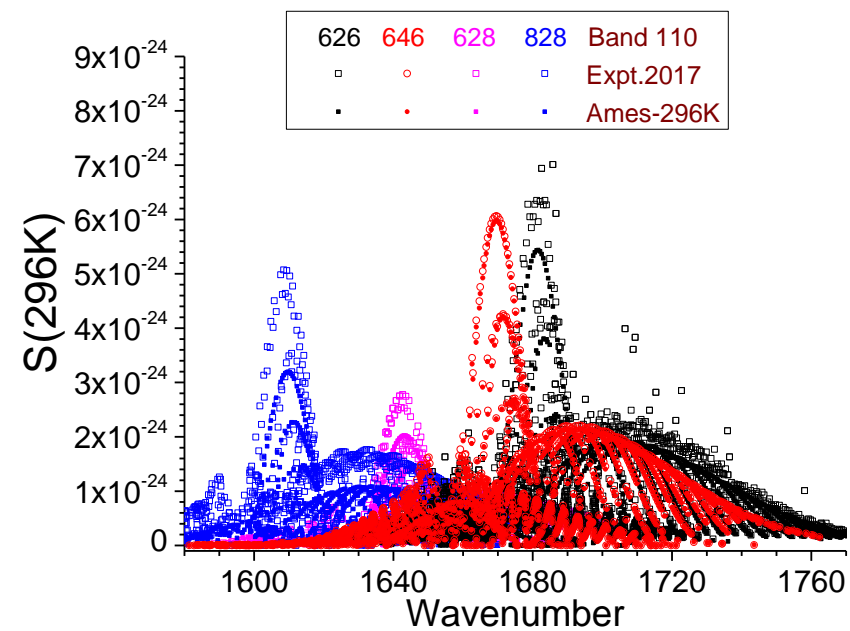
Fig.3 (a-b) Single J contribution, accumulated 0- J contribution, and the missing part of SO₂ 626 partition sum, divided by Q_{Total} at 296K or 750K. $J=0-150$ calculations were carried out on Ames-Pre2 PES, eigenvalues are cutoff at 8347 cm⁻¹ above the ZPE. (c) Left: Partition contribution from energy levels in each 100 cm⁻¹ (black squares); Right: relative weight for every 100 cm⁻¹ contribution (blue triangles); and the Q_{Total} defect, “missing” weight (blue circles). Solid symbols for 296K, open symbols for 750K.



(a)



(b)



(c)

Fig.4 (a) Isotopologue consistency of Ames Transition Dipole Moments (TDM) for pure rotational band and 3 combinational bands, the values are divided by the TDM of main isotopologue (626); (b) the $\nu_2+\nu_3$ (011) band intensity agreements between Ames vs. Expt.[12], compare to those $\delta\%$ of $\nu_1+\nu_2$ (110) band in the in-set panel; (c) the $\nu_1+\nu_2$ (110) band intensity of Ames (solid dots) and Expt.(open squares).[12]

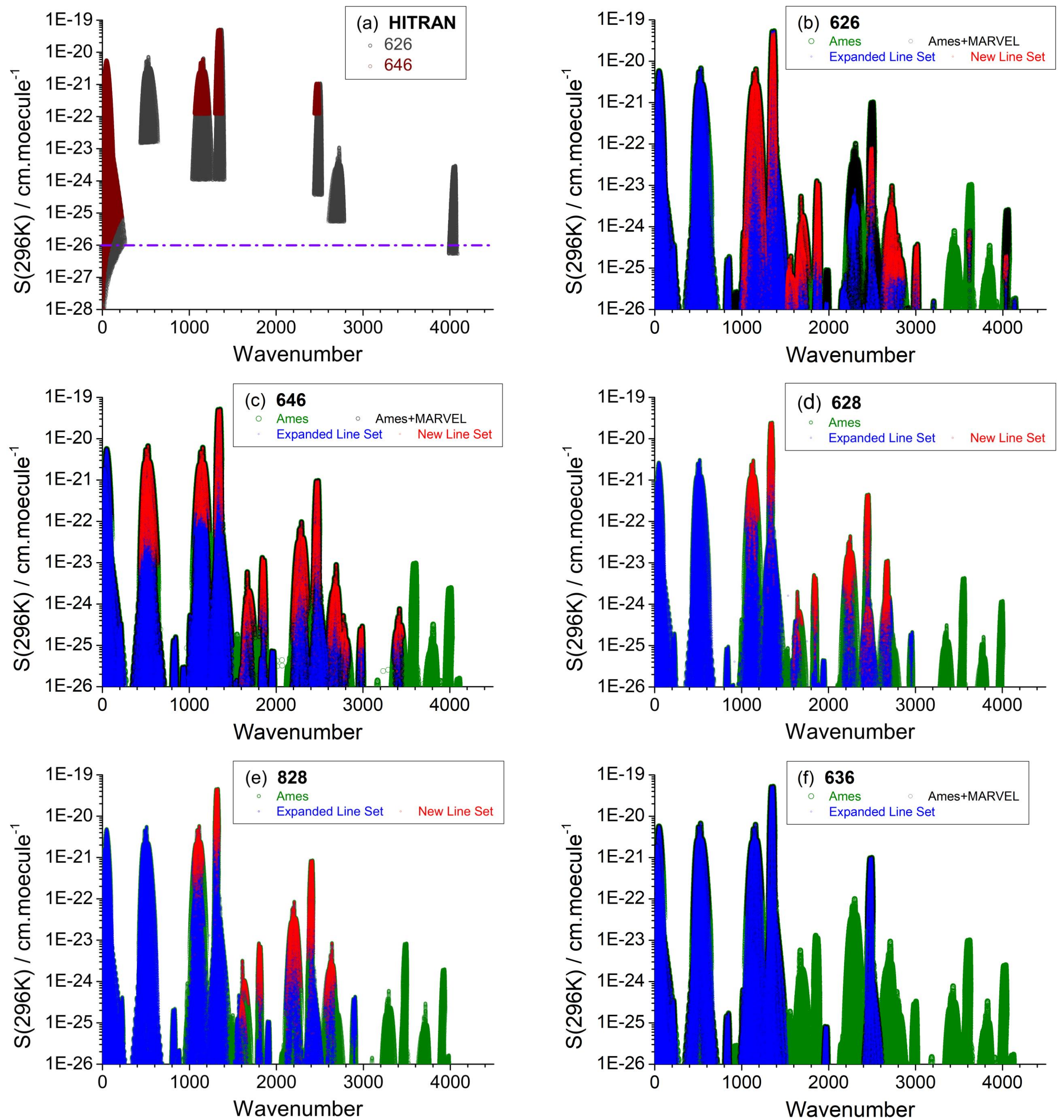


Fig.5 Data coverage of HITRAN (a), the New Line sets (b-e, red dots), the Expanded line sets (b-f, blue dots), the Ames+MARVEL line sets (b,c,f, black dots, shadowed by blue dots). The green dots (Ames-296K intensity, $J''/K_a'' \leq 50/25$) not covered by other line sets indicate the missing bands below 4500 cm^{-1} .